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Communication

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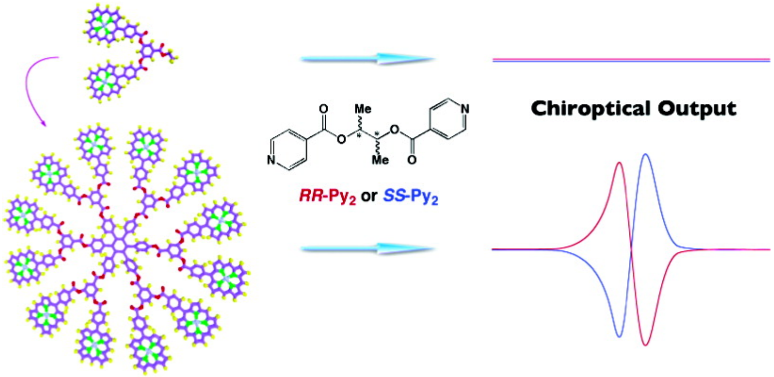

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Cooperativity in Chiroptical Sensing with Dendritic Zinc Porphyrins

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Dendrimers are regularly branched three-dimensional macromolecules, whose properties are dependent on the numbers of generation and branch units, along with the structures of building blocks, surface groups, and core modules.[1] Site-selective positioning of functional groups in dendritic architectures is expected to induce cooperative phenomena that may lead to a significant enhancement of certain functions. Examples of such cooperative phenomena with dendritic macromolecules have been reported for catalysis,[2] molecular recognition and inclusion,[3] and light harvesting.[4] We are motivated to explore the potential utility of such a cooperative phenomenon for sensory applications. Here, we report the synthesis of a series of dendritic macromolecules functionalized with multiple zinc porphyrin units (Chart 1) and highlight a clear cooperative effect on chiroptical sensing of an asymmetric ligating molecule.

Certain zinc porphyrin dimers are known to be useful for chiroptical sensing of asymmetric compounds,[5] where the clockwise or counterclockwise-twisted geometry of the zinc porphyrin dimers is generated by ligation with chiral guests and displays an exciton-coupled circular dichroism (CD) in the visible region. Thus, we chose two- and three-branched zinc porphyrins, $\mathbf{2P_{Zn}}$ and $\mathbf{3P_{Zn}}$ (Chart 1), respectively, as the sensory parts attached to the termini of hexaarylbenzene-anchored polyester dendrimers ($\mathbf{12P_{Zn}}$/$\mathbf{24P_{Zn}}$ and $\mathbf{18P_{Zn}}$/$\mathbf{36P_{Zn}}$) and investigated their sensing capabilities toward $\mathbf{Py_2}$, a chiral bidentate guest. These metalloporphyrin-appended dendrimers were unambiguously characterized by several analytical methods.[6,7] Two-branched $\mathbf{2P_{Zn}}$, upon titration with *RR*-$\mathbf{Py_2}$ or *SS*-$\mathbf{Py_2}$ (Chart 1) in $CHCl_3$, did not show any induced CD (ICD) bands at 25 °C.[6] On the other hand, three-branched $\mathbf{3P_{Zn}}$ exhibited a certain ICD response under conditions identical to those above.[6]

We found that $\mathbf{12P_{Zn}}$ and $\mathbf{24P_{Zn}}$, having $\mathbf{2P_{Zn}}$ units on the dendritic scaffolds, both exhibit a strong ICD response toward the enantiomers of $\mathbf{Py_2}$. For example, when a $CHCl_3$ solution of $\mathbf{24P_{Zn}}$ (0.21 μM) was titrated with *RR*-$\mathbf{Py_2}$ at 25 °C, the Soret and Q-bands of $\mathbf{24P_{Zn}}$ at 414.4 and 543.2 nm were red-shifted to 419.0 and 550.4 nm, respectively, with isosbestic points at 412.8 and 545.6 nm (Figure 1a).[6] Thus, $\mathbf{24P_{Zn}}$ can accommodate *RR*-$\mathbf{Py_2}$, where the association constant evaluated ($K_{assoc} = 4.0 \times 10^4$ M^{-1}; Figure 2a) is nearly 40-times as large as that of $\mathbf{2P_{Zn}}$ ($K_{assoc} = 1.0 \times 10^3$ M^{-1}).[6] Upon complexation with *RR*-$\mathbf{Py_2}$, $\mathbf{24P_{Zn}}$ displayed an intense positive split Cotton effect at the Soret absorption band of the zinc porphyrin units (Figure 1b, red curve). When *SS*-$\mathbf{Py_2}$ was used in place of *RR*-$\mathbf{Py_2}$, $\mathbf{24P_{Zn}}$ exhibited a perfect mirror-image CD spectrum (blue curve) of that with *RR*-$\mathbf{Py_2}$. The large chiroptical response of $\mathbf{24P_{Zn}}$ is originating from a twisted geometry of the guest-binding zinc porphyrin dyads on the dendrimer scaffold. In contrast, toward *RR*-$\mathbf{Py}$, a chiral monodentate analogue of *RR*-$\mathbf{Py_2}$, $\mathbf{24P_{Zn}}$, displayed a much lower affinity ($K_{assoc} = 4.2 \times 10^2$ M^{-1}) and hardly showed a chiroptical response even upon addition of a large excess of *RR*-$\mathbf{Py}$ (3.4×10^5 equiv; black curve).[6] Thus, $\mathbf{Py_2}$ actually serves as a bidentate ligand. As expected, complexation of $\mathbf{24P_{Zn}}$ with achiral *meso*-$\mathbf{Py_2}$ ($K_{assoc} = 4.0 \times 10^4$ M^{-1}) did not result in any chiroptical response (green curve).[6]

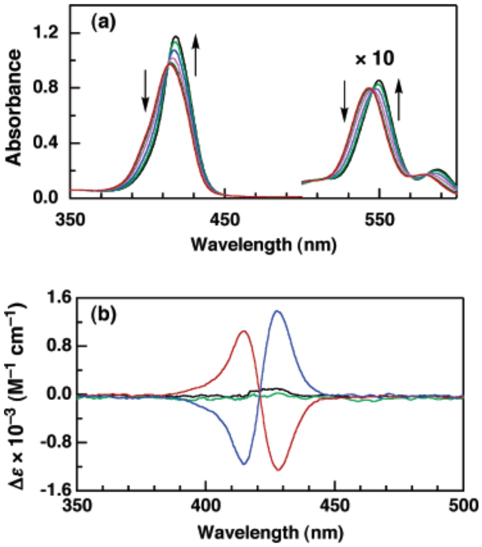

Figure 1. (a) Absorption spectral change of $\mathbf{24P_{Zn}}$ (0.21 μM) upon titration with *RR*-$\mathbf{Py_2}$ ([*RR*-$\mathbf{Py_2}$]/[$\mathbf{24P_{Zn}}$] = 1, 6, 29, 116, 473, and 1903) in $CHCl_3$ at 25 °C. (b) Circular dichroism (CD) spectra of $\mathbf{24P_{Zn}}$ in the presence of *RR*-$\mathbf{Py_2}$ (red curve), *SS*-$\mathbf{Py_2}$ (blue curve), *meso*-$\mathbf{Py_2}$ (green curve) ([guest]/[$\mathbf{24P_{Zn}}$] = 1000), and *RR*-$\mathbf{Py}$ (black curve) ([guest]/[$\mathbf{24P_{Zn}}$] = 340 000) in $CHCl_3$ at 25 °C.

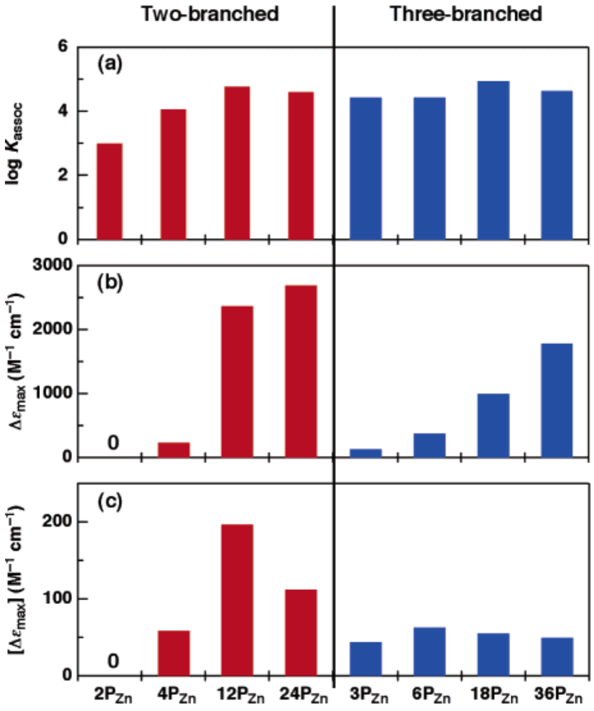

Figure 2. (a) Association constants (log K_{assoc}), (b) maximum CD amplitudes ($\Delta\epsilon_{max}$), and (c) contributions of each zinc porphyrin unit to $\Delta\epsilon_{max}$ ([$\Delta\epsilon_{max}$]) for dendrons $\mathbf{4P_{Zn}}$ and $\mathbf{6P_{Zn}}$, and dendrimers $\mathbf{12P_{Zn}}$, $\mathbf{18P_{Zn}}$, $\mathbf{24P_{Zn}}$, and $\mathbf{36P_{Zn}}$, along with their precursors $\mathbf{2P_{Zn}}$ and $\mathbf{3P_{Zn}}$ in $CHCl_3$ at 25 °C in the presence of *RR*-$\mathbf{Py_2}$.

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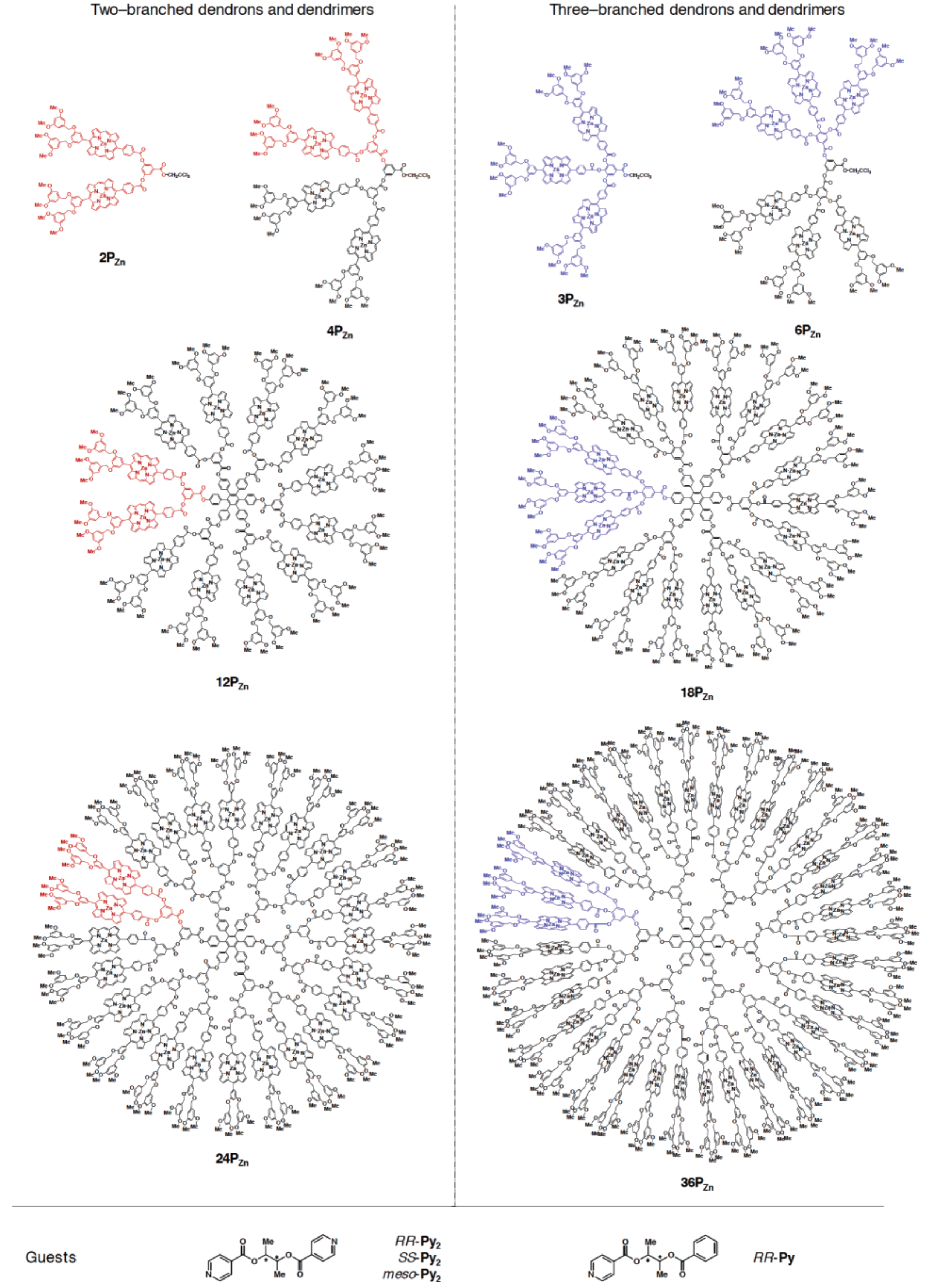
Chart 1. Schematic Structures of Zinc Porphyrin-Appended Dendrons and Dendrimers Together with Guests



We also found that the capability of chiroptical sensing is highly dependent on the generation number of the dendrimer scaffold. From a spectroscopic titration with *RR*-$\mathbf{Py_2}$ in $CHCl_3$ at 25 °C, the K_{assoc} value of one-generation lower $\mathbf{12P_{Zn}}$ (6.0×10^4 M^{-1}) was evaluated to be almost comparable to that of **24P$_{Zn}$** (Figure 2a). The maximum CD amplitude[8] observed for **12P$_{Zn}$** ($\Delta\epsilon_{max} = 2363$ M^{-1} cm^{-1}) in the presence of *RR*-**Py$_2$** was smaller than that for **24P$_{Zn}$** (2693 M^{-1} cm^{-1}) (Figure 2b). However, when these values were divided by the numbers of the zinc porphyrin units, one may note that the contribution of each chromophore (**P$_{Zn}$**) unit in **12P$_{Zn}$** to $\Delta\epsilon_{max}$ ($[\Delta\epsilon_{max}] = 196$ M^{-1} cm^{-1}) is much greater than that in **24P$_{Zn}$** (112 M^{-1} cm^{-1}) (Figure 2c). In contrast with **2P$_{Zn}$**, a dendron such as **4P$_{Zn}$** ($K_{assoc} = 1.1 \times 10^4$ M^{-1}) exhibited a chiroptical response toward *RR*-**Py$_2$**; however, $[\Delta\epsilon_{max}]$ was only 59 M^{-1} cm^{-1}, definitely smaller than those of **12P$_{Zn}$** and **24P$_{Zn}$**. These observations indicate a possible cooperative function of the zinc porphyrin units in **12P$_{Zn}$** and **24P$_{Zn}$** for chiroptical sensing.

In sharp contrast, the zinc porphyrin units in dendrimers **18P$_{Zn}$** and **36P$_{Zn}$** did not show any cooperativity in chiral recognition, although precursor **3P$_{Zn}$** itself ($K_{assoc} = 2.7 \times 10^4$ M^{-1}) exhibits a certain chiroptical response toward **Py$_2$**. Spectroscopic titration profiles of **18P$_{Zn}$** and **36P$_{Zn}$** with *RR*-**Py$_2$** in $CHCl_3$ at 25 °C were virtually identical to those of **12P$_{Zn}$** and **24P$_{Zn}$**, and gave comparable K_{assoc} values of 8.9×10^4 and 4.4×10^4 M^{-1}, respectively (Figure 2a). As shown in Figure 2b, the magnitudes of $\Delta\epsilon_{max}$ (M^{-1} cm^{-1}), upon complexation with *RR*-**Py$_2$**, are in the following order: **3P$_{Zn}$** (131), **18P$_{Zn}$** (996), and **36P$_{Zn}$** (1781). However, the $[\Delta\epsilon_{max}]$ values (M^{-1} cm^{-1}) of **18P$_{Zn}$** (55) and **36P$_{Zn}$** (49) are almost comparable to that of **3P$_{Zn}$** (43) (Figure 2c). Reference dendron **6P$_{Zn}$** ($K_{assoc} = 2.7 \times 10^4$ M^{-1}) showed a $[\Delta\epsilon_{max}]$ value of 63 M^{-1} cm^{-1}, which again hardly differs from that of precursor **3P$_{Zn}$**.

As described in the above two sections, the K_{assoc} values of the **2P$_{Zn}$** series (Figure 2a, red bars) show a certain superiority of the dendrimers over the dendrons in guest binding, but the binding capabilities of dendrimers **12P$_{Zn}$** and **24P$_{Zn}$** are not much different from one another. In contrast, such a structural dependence can hardly be seen in the K_{assoc} values of the **3P$_{Zn}$** series (Figure 2a, blue bars). On the other hand, a more explicit difference between these two series can be seen in their chiroptical responses (Figure 2c). The $[\Delta\epsilon_{max}]$ values of the **2P$_{Zn}$** series (red bars) show that **12P$_{Zn}$** is the better-behaved chiroptical sensor than the other, indicating the presence of an optimum structure for chiral recognition. On the other hand, the chiroptical sensing capabilities of the **3P$_{Zn}$** series (blue bars) hardly depend on the structure of the dendritic scaffold, and they are all much lower than that of **12P$_{Zn}$**. Thus, both for the guest binding and for chiroptical sensing, the zinc porphyrin units in the **2P$_{Zn}$** series, rather than those in the **3P$_{Zn}$** series, can function cooperatively.

The above trends may be related to the intramolecular interaction among the zinc porphyrin units. Thus, we conducted absorption spectroscopy in $CHCl_3$ at 25 °C.[6] **2P$_{Zn}$** showed a narrower Soret band than **3P$_{Zn}$** (fwhm [full width at half-maximum] = 943 and 1305 cm^{-1}, respectively), indicating a weaker ground-state interaction among the zinc porphyrin units in **2P$_{Zn}$**. While dendrons **4P$_{Zn}$** (927 cm^{-1}) and **6P$_{Zn}$** (1284 cm^{-1}) were almost comparable to the corresponding precursors in terms of fwhm, the dendrimers displayed a much broader Soret band than these smaller homologues.[6] In particular, **12P$_{Zn}$** and **18P$_{Zn}$** clearly displayed a blue-shifted shoulder in the Soret absorption region, while **24P$_{Zn}$** and **36P$_{Zn}$** only showed broadening of the Soret band without any detectable shifts (fwhm = 1558 and 2031 cm^{-1}, respectively). Of much interest, the major Soret band of **12P$_{Zn}$** was entirely blue-shifted by 3.8 nm from that of **2P$_{Zn}$**, while such a blue shift was obviously smaller for **18P$_{Zn}$** (1.4 nm from the Soret band of **3P$_{Zn}$**). From these spectral features, we assume that **12P$_{Zn}$** most likely possesses an efficient H-aggregated overlap of the zinc porphyrin units by a head-to-tail interaction among the neighboring **2P$_{Zn}$** dyads. Thanks to a smaller steric congestion of **12P$_{Zn}$** than the other dendrimers, such H-aggregated dyads may flexibly twist their conformation to accommodate the chiral guests, thereby displaying a large ICD response in the visible region.

Chiroptical sensing of asymmetric compounds is a subject of increasing importance for biological and medicinal applications. Here, we demonstrated a cooperative function of multiple zinc porphyrin units on the dendrimer scaffold for efficient translation of chiral information. Utilization of the resulting supramolecular chirality for asymmetric catalysis is one of the subjects worthy of further investigations.

Supporting Information Available: Details for synthesis, characterization, and spectral data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) See Supporting Information.

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(8) Upon titration, the CD intensity initially increased up to a maximum value and then decreased when the guest concentration exceeded a certain point, suggesting a competition of bridging versus nonbridging ligations.

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